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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference RSJ07615WO	**FOR FURTHER ACTION** See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB 03/04322	International filing date *(day/month/year)* 08.10.2003	Priority date *(day/month/year)* 08.10.2002
International Patent Classification (IPC) or both national classification and IPC G01N33/00		
Applicant CITY TECHNOLOGY LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand 20.04.2004	Date of completion of this report 26.10.2004
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Joyce, D Telephone No. +31 70 340-3093

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB 03/04322

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1, 3-11	as originally filed
2	filed with telefax on 28.09.2004

Claims, Numbers

14-17	as originally filed
1-13	filed with telefax on 28.09.2004

Drawings, Sheets

1/9-9/9	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-17
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-17
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-17
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US-A-6 046 054 (DAWSON DARRYL HIRST ET AL) 4 April 2000 (2000-04-04)

D2: WO 93/08467 A (CAPTEUR SENSORS & ANALYSERS) 29 April 1993 (1993-04-29)

D3: WO 01/38867 A (CAPTEUR SENSORS ANS ANALYSERS ;KING CHARLES EDMUND (GB); SMITH PET) 31 May 2001 (2001-05-31)

D4: EP-A-1 008 847 (SIEMENS AG) 14 June 2000 (2000-06-14)

D5: EP-A-1 041 039 (IMRA EUROP SA) 4 October 2000 (2000-10-04)

D6: WO 95/00836 A (CAPTEUR SENSORS & ANALYSERS ;MCGEEHIN PETER (GB); MOSELEY PATRICK) 5 January 1995 (1995-01-05)

Article 33 PCT:

1.0 The document D1 is regarded as being the closest prior-art to the subject-matter of independent claims 1 and 10 and discloses (the references in parentheses applying to this document):
A method of detecting a predetermined alarm condition in a combustion emission gas (Col 1line 61-65), exposing to the gas a semiconductor gas sensor having a p- type semiconducting material (Col 1 line 66-Col 2 line 8), the semiconducting material exhibiting an increase in its electrical resistance in response to an increase in concentration of a reducing gas in the surrounding atmosphere (Col 5 line 66-Col 6 line 1) monitoring the resistance (Fig:6); and outputting an alarm signal if the resistance exceeds a predetermined value corresponding to the alarm condition (Col 1 line 61-65).

1.1 The subject-matter of claims 1 and 10 therefore differs from this known document D1 in that:
The p-type semiconducting sensor material of the present application exhibits a combined resitance increase upon a decrease in the concentration of oxygen coupled witha resistance increase upon an increase in carbon monoxide concentration.

Subsequently the subject-matter of independent claims 1 and 10 is deemed to be novel in the sense of Article 33(2) PCT.

1.2 The problem to be solved by the present invention may therefore be regarded as how to provide an alarm condition response from a single semiconducting sensor for

both reducing and oxidising gaseous environments.

1.3 The present inventors have found that a p-type semiconducting sensor material can posses a rapid and reversible resistance increase in response to both to an increase in carbon monoxide concentration and a decrease in oxygen concentration, providing a single sensor which outputs an alarm condition indication when the flue boiler air supply drops or when there is incomplete combustion, thus the sensor will detect the condition as a result of this combined effect.

1.4 None of the cited &/or consulted prior-art documents acknowledges the above problem nor does it suggest the present solution. The prior-art teachings are commonly concerned with oxygen and carbon monoxide detection with p-type semiconducting mixed metal oxides with multiple sensors sensitive to each particular gas. None of the prior-art teachings gives an indication of a combined sensor signal, exhibiting a resistance increase towards an increase in carbon monoxide and a decrease in oxygen. Hence the independent claims 1 and 10 of the present application are seen to involve an inventive step in the sense of Article 33(3) PCT.

1.5 Dependent claims 2-9 and 11-17 respectively define further refinements of the new and inventive idea underlying independent claims 1 and 10, and therefore also meet the requirements of Article 33 PCT for the same reasons as given above.

1.6 The industrial applicability of the independent claims 1 and 10 is immediately evident, so that therefore all the requirements of Article 33 PCT are met.

these other undesirable circumstances, this will confer further advantage. Although the primary application addressed here is that of a safety alarm activated in the event of malfunction, it will also be clear that one or more of these conditions may also be used to act as a control parameter to ensure safe and efficient operation of the combustion plant.

WO-A-93/08467 and US-A-6046054 disclose a gas sensor for detecting more than one gas but this requires separate sensing elements.

In accordance with a first aspect of the present invention, a method of detecting a predetermined alarm condition in a combustion emission gas comprises exposing to the gas a semiconductor gas sensor having a p-type semiconducting material, the semiconducting material exhibiting an increase in its electrical resistance in response to an increase in concentration of a reducing gas in the surrounding atmosphere and in response to a decrease in concentration of oxygen in the surrounding atmosphere; monitoring the resistance; and outputting an alarm signal if the resistance exceeds a predetermined value corresponding to the alarm condition.

In accordance with a second aspect of the present invention, a combustion emission gas alarm system comprises a semiconductor gas sensor having a p-type semiconducting material, the semiconducting material exhibiting an increase in its electrical resistance in response to an increase in concentration of a reducing gas in the surrounding atmosphere and in response to a decrease in concentration of oxygen in the surrounding atmosphere; and apparatus for monitoring the resistance of the semiconducting material and for issuing an alarm signal if the resistance exceeds a predetermined value corresponding to an alarm condition.

Thus we use a semiconductor material which will sense oxygen, a reducing gas, or both in contrast to WO-A-93/08467 where separate sensors are required.

CLAIMS

1. A method of detecting a predetermined alarm condition in a combustion emission gas, the method comprising exposing to the gas a semiconductor gas sensor having a p-type semiconducting material, the semiconducting material exhibiting an increase in its electrical resistance in response to an increase in concentration of a reducing gas in the surrounding atmosphere and in response to a decrease in concentration of oxygen in the surrounding atmosphere; monitoring the resistance; and outputting an alarm signal if the resistance exceeds a predetermined value corresponding to the alarm condition.

2. A method according to claim 1, wherein the reducing gas is one of CO, H_2, CH_4 and higher hydrocarbons.

3. A method according to claim 1 or claim 2, wherein the electrical resistance of the semiconductor gas sensor is related to the concentrations of oxygen and carbon monoxide in the surrounding atmosphere over at least a range of atmospheric compositions via an expression of the form:

$$R_G = A[O_2]^{-1/x} + B[O_2]^{-1/x}[CO]^{1/2}$$

where :

R_G is the observed sensor resistance

$[O_2]$ is the oxygen concentration

[CO] is the carbon monoxide concentration

A, B are constants which depend on the sensor resistance under reference conditions

x is a parameter which depends on the point defect chemistry of the oxide system.

4. A method according to any of the preceding claims, wherein the p-type material comprises a metal oxide.

5. A method according to any of claims 1 to 3, wherein the p-type material comprises a mixed metal oxide.

6. A method according to claim 4 or claim 5, wherein the metal is of the first, second and/or third order transition metal series.

7. A method according to claim 6, wherein the semiconductor material comprises a p-type oxide of the Cr-Ti-O system.

8. A method according to claim 6, wherein the semiconductor material comprises a p-type Cr-Ti-Mn-O system, CuO with TiO_2 or CoO with TiO_2.

9. A method according to any of the preceding claims, wherein the combustion emission gas is a flue gas.

10. A combustion emission gas alarm system comprising a semiconductor gas sensor having a p-type semiconducting material, the semiconducting material exhibiting an increase in its electrical resistance in response to an increase in concentration of a reducing gas in the surrounding atmosphere and in response to a decrease in concentration of oxygen in the surrounding atmosphere; and apparatus for monitoring the resistance of the semiconducting material and for issuing an alarm signal if the resistance exceeds a predetermined value corresponding to an alarm condition.

11. A system according to claim 10, wherein the electrical resistance of the semiconductor gas sensor is related to the concentrations of oxygen and carbon monoxide in the surrounding atmosphere over at least a range of atmospheric compositions via an expression of the form:

$$R_G = A[O_2]^{-1/x} + B[O_2]^{-1/x}[CO]^{1/2}$$

where :

R_G is the observed sensor resistance

$[O_2]$ is the oxygen concentration

$[CO]$ is the carbon monoxide concentration

A, B are constants which depend on the sensor resistance under reference conditions

x is a parameter which depends on the point defect chemistry of the oxide system.

12. A system according to claim 10 or claim 11, wherein the p-type material comprises a metal oxide.

13. A system according to claim 10 or claim 11, wherein the p-type material comprises a mixed metal oxide.